

Measurement of the Capillary Length for the Dendritic Growth of Ammonium Chloride

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Abstract

We report the results of a new method of measuring the capillary length for the dendritic crystal growth of non-faceted materials. This method uses a nearly spherical crystal held near unstable equilibrium in an oscillating temperature field. For the growth of ammonium chloride crystals from aqueous solution, previous published estimates varied by over a factor of 20. With this new method, we find a capillary length d_0 of 0.224 ± 0.005 nm, similar to that obtained for ammonium bromide crystals.

Keywords: A1.Dendrites, A1.Supersaturated solutions, A1.Growth models

1. Introduction

Dendritic crystal growth is a common form of solidification observed for the diffusion-limited growth of non-faceted materials. It is important technologically because many metals and metal alloys solidify in dendritic patterns, but it is also of more general interest as one of the standard examples of pattern formation in a nonlinear, nonequilibrium system [1]. For reviews, see Boettinger et al. [2] and Glicksman and March [3].

In the standard model of diffusion limited growth, there are two characteristic length scales [1]. One is the diffusion length l , given by $l = 2D/v$, where D is the relevant diffusion constant and v is interface velocity. The other is the capillary length, d_0 , which is related to the energy of the solid-liquid interface. For a pure system, d_0 is given by

$$d_0 = \gamma T_M c_p / L^2 \quad (1)$$

where γ is the solid-liquid surface tension, T_M is the melting temperature for a flat interface, c_p is the specific

heat per unit volume, and L is the latent heat per unit volume.

For growth from solution, d_0 is given by

$$d_0 = \frac{\gamma}{(\Delta C)^2} \frac{\partial \mu}{\partial C} \quad (2)$$

where ΔC is the difference in concentration between the solid and liquid phases, and μ is the chemical potential.

For a few simple pure materials, such as helium [4] or xenon [5], it is possible to measure the materials constants in Eq. 1 directly and thus determine d_0 . More commonly, however, d_0 must be determined from measurements of the solid-liquid interface shape under well-controlled experimental conditions.

For pure materials, or for dilute solutions, Schaefer, Glicksman, and Ayers [6] showed how to use measurements of the curvature of the solid-liquid interface near a grain boundary to determine d_0 , and applied the technique to succinonitrile. Glicksman and Singh [7] applied the same technique to pivalic acid. Similar measurements have been made for xenon [8] and pyrene [9]. Luo, Strachan, and Swift [10] developed a method to use the maximum supercooling obtainable for a pure system to determine the solid-liquid interfacial energy, and applied it to the ice-water system.

For growth from solution, Dougherty and Gollub [11] modeled the shrinking of a nearly spherical crystal of

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ammonium bromide. Tanaka and Sano [12] and Sawada et al. [13] applied the same technique to ammonium chloride. Gomes, Falcão, and Mesquita [14] used the instability of a cellular interface to measure the capillary length for a nematic-isotropic interface in liquid crystals.

For ammonium bromide, Dougherty and Gollub [11] estimated $d_0 = 0.28\text{nm}$. For ammonium chloride, Tanaka and Sano [12] estimated a much larger value of $d_0 = 1.59 \pm 0.06\text{nm}$, while Sawada et al. [13] estimated a much smaller value of $d_0 = 0.065\text{nm}$.

In this paper, we extend the method of Ref. [11] to maintain a nearly spherical crystal of ammonium chloride close to a state of unstable equilibrium, and extract a value for d_0 from the quasistatic growth and shrinking of that crystal. Our final result of 0.22nm is intermediate between the two previous results, and is also comparable to our previously-reported value for ammonium bromide.

2. Theory

The theory for diffusion-limited growth of an isotropic spherical crystal in an isothermal solution is developed in Ref. [1]. The central result used here is that the radial growth velocity, dR/dt , is given by

$$\frac{dR}{dt} = \frac{D}{R} \left(\Delta - \frac{2d_0}{R} \right) \quad (3)$$

where R is the radius of the crystal, D is the diffusion coefficient for NH_4Cl in aqueous solution, d_0 is the capillary length, and Δ is the dimensionless supersaturation, given in Ref. [1] by

$$\Delta = \frac{\mu(T) - \mu_{eq}}{\Delta C(\partial\mu/\partial C)}$$

In this experiment, the typical temperature variations are less than $\pm 0.02^\circ\text{C}$, so we adopt a simple linear model for Δ , namely

$$\Delta = c_T(T_{eq} - T) \quad (4)$$

where T_{eq} is the temperature at which a flat interface would be in equilibrium, and c_T is to be determined empirically.

The diffusion coefficient for lower concentrations and temperatures was measured by Lutz and Mendenhall [15] and by Hall, Wishaw, and Stokes [16]. Extrapolating those published values to the temperatures and concentrations used in this work, we estimate $D = 2500\mu\text{m}^2/\text{s}$, similar to the values of $2600\mu\text{m}^2/\text{s}$ used by Tanaka and Sano [12], and $2280\mu\text{m}^2/\text{s}$ used by Sawada

et al. [13]. For this experiment, where the crystal rests against the bottom plate of the growth cell, we estimate the effective diffusion constant to be $0.71D$ [11, 12].

3. Experiments

The experiments were performed with aqueous solutions of ammonium chloride with approximately 40% NH_4Cl by weight. The saturation temperature was approximately 80°C . The solution was placed in a $40 \times 10 \times 2\text{ mm}$ glass spectrophotometer cell sealed with a Teflon stopper held in place by epoxy. A thermistor was mounted on the cell for direct readings of the temperature near the crystal. The cell was mounted in a massive copper block, surrounded by an insulated outer aluminum block, and placed on a microscope enclosed in an insulating box.

The temperature of the outer aluminum block was controlled to approximately $\pm 0.1^\circ\text{C}$. The temperature of the inner copper block was controlled directly by computer, allowing complete programmatic control over the temperature during the course of a run. The temperature of the sample was stable to within approximately $\pm 5 \times 10^{-4}^\circ\text{C}$.

Images were obtained from a charged coupled device (CCD) camera attached to the microscope and acquired directly into the computer via a Data Translation DT3155 frame grabber with a resolution of 640×480 pixels. The ultimate resolution of the images was $0.314 \pm 0.005\mu\text{m}/\text{pixel}$.

To obtain a single crystal, the solution was heated to dissolve all the NH_4Cl , stirred to eliminate concentration gradients, and then cooled to initiate growth. Many crystals would nucleate, but an automated process was set up to acquire images and slowly adjust the temperature until only a single isolated crystal remained.

The interface position and radius of the nearly spherical crystals were measured as in Ref. [17]. The temperature was then continually adjusted until this crystal was the desired size. Although such a spherical crystal is in a state of unstable equilibrium, we found it possible to maintain it indefinitely, provided we continually monitored the size and adjusted the temperature accordingly. This isolated, nearly spherical, crystal was allowed to stabilize for several days, and is shown in Fig. 1.

Once a single, stable crystal was obtained, the temperature of the sample was slowly oscillated with an amplitude of 0.0125°C and a period of 1 hour. This caused the crystal to alternatively grow and dissolve slowly, such that there was plenty of time for the system to attain thermal equilibrium, but the size and growth rate

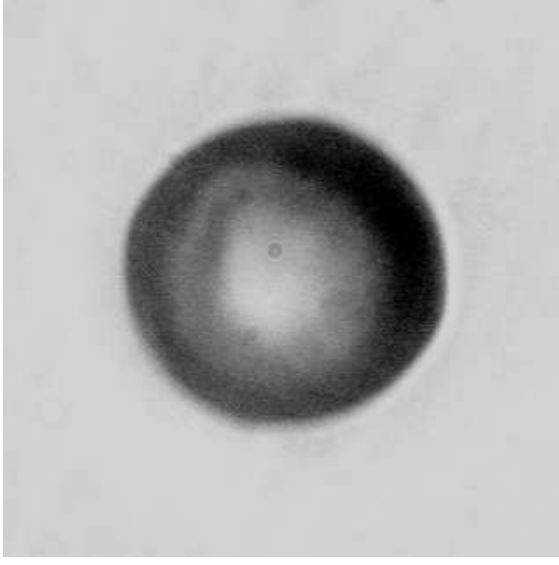


Figure 1: Crystal of ammonium chloride held in unstable equilibrium. The image is $100\ \mu\text{m}$ across.

changed enough that both terms on the right of Eq. 3 were significant.

We then used the data for $T(t)$ to numerically integrate Eq. 3 and compare to the measured $R(t)$. We determined the constants c_T , T_{eq} , and d_0 in Eqs. 3 and 4 by minimizing χ^2 , the squared difference between the integrated prediction and the measured values for $R(t)$. Since both c_T and d_0 are ultimately multiplied by D in Eq. 3, these measurements only constrain the products Dc_T and Dd_0 . For simplicity, and for consistency with Refs. [11, 12, 13], we have assumed an extrapolated value for D , but this experiment provides no independent confirmation of that value.

3.1. Results

The results are shown in Fig. 2. The best fit parameters are $d_0 = (2.24 \pm 0.05) \times 10^{-4}\ \mu\text{m}$, $c_T = (4.23 \pm 0.01) \times 10^{-3}/^\circ\text{C}$, and $T_{eq} = 80.70 \pm 0.01^\circ\text{C}$. A second run on a different crystal gave consistent results.

This value compares favorably with the value of $2.8 \times 10^{-4}\ \mu\text{m}$ previously reported for NH_4Br [11], and is in between the values for NH_4Cl reported in Refs. [12] and [13].

With this value of d_0 , we can also make an updated estimate for the stability constant σ^* , defined by

$$\sigma^* = \frac{2d_0D}{v\rho^2}$$

Based on the previously reported [18] value of $v\rho^2 = 12 \pm 2\ \mu\text{m}^3/\text{s}$, we estimate $\sigma^* = 0.093 \pm 0.016$ for growth

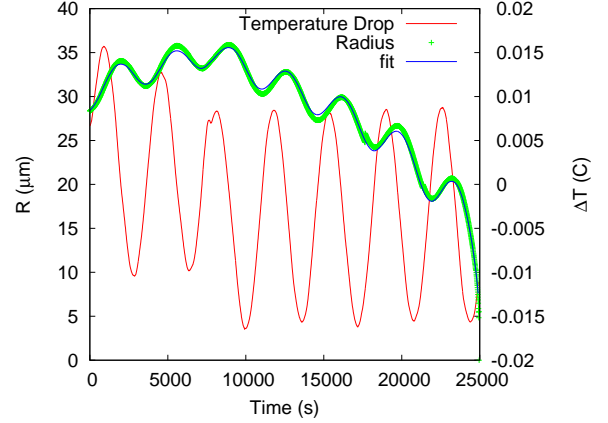


Figure 2: Measured (dots) and fit (line) values for the radius as a function of time of an oscillating crystal. The driving temperature variations ΔT are shown with a dashed line (red online).

at small supersaturation.

There were two main factors we found to be important in getting consistent results from this experiment. First, control and measurement of the temperature at the sample was critical. In preliminary trials with poorer insulation, or where we measured the temperature of the surrounding copper block instead of the sample cell, we were unable to get satisfactory fits to Eq. 3 over long time scales as in Fig. 2.

Second, the oscillating protocol proved a robust probe of Eq. 3. In previous work on slowly dissolving crystals, as in Ref. [11], we typically found that the fitted value for d_0 depended very sensitively on the last few data points, where the crystal was shrinking rapidly just before completely dissolving. Small drifts in temperature on the order of $\pm 0.001^\circ\text{C}$ could make significant differences in the quality of the fit. In Ref. [12], the fit does not include the last two data points, though it is not clear why. By contrast, Fig. 2 includes both growing and dissolving segments so that both terms in Eq. 3 were significant, and the fit was well-constrained.

One remaining uncertainty is the possible role of convection in this experiment. The density differences caused by the growth and dissolution of the crystal could drive small convection currents. However, the excellent fit to the data suggests that Eq. 3 still provides an effective model for the growth process.

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